Effect of molecular reorientation on excitation decay due to incoherent energy transfer

Knoester, J.; Van Himbergen, J. E.

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Effect of molecular reorientation on excitation decay due to incoherent energy transfer

J. Knoester and J. E. Van Himbergen
Institute for Theoretical Physics, University of Utrecht, Princetonplein 5, P. O. Box 80.006, 3508TA Utrecht, The Netherlands

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A complete study is presented of the excitation decay $\rho(t)$ due to incoherent energy transfer in a system of randomly distributed donor molecules, following a flash excitation at $t = 0$. In particular the dipole–dipole interaction is considered, which causes the well-known anisotropic Förster transfer, and thus makes the transfer process sensitive to molecular reorientations. The general case of a finite reorientation time scale τ_a and an arbitrary orientational distribution is considered here, from which the static and dynamic limits are obtained as limiting cases for $\tau_a \to \infty$ and $\tau_a \to 0$, respectively, for arbitrary degree of orientational order. In the isotropic case, these reduce to well-known results. In our approximation the influence of reorientational motion on $\log \rho(t)$ can be fully contained in a time dependent factor $g(t/\tau_a)$. From a general expression, $g(t/\tau_a)$ is evaluated for the isotropic case by numerical techniques for different models of reorientation, viz. reorientation through large uncorrelated steps and diffusion type reorientation. By means of a rigorous scaling procedure of t, based on the exact expression of $g(t/\tau_a)$ for small t/τ_a, it is shown, that in principle, experimental determination of $g(t)$ can be used to estimate τ_a and determine the amount of diffusive behavior in the reorientational motion.

I. INTRODUCTION

For many years there has been great interest in phenomena related to incoherent radiationless transfer of energy between donor and acceptor molecules embedded in a host medium.[1] Nevertheless, one aspect of this problem, the effect of molecular reorientations on various quantities of interest, has received relatively little attention. In fact, usually only two limiting situations have been considered explicitly: molecular reorientations occur either very frequently (dynamic limit) or hardly at all (static limit) on time scales characteristic for energy transfer. And even in these limits, rigorous results only exist for the case of a uniform distribution over all possible molecular orientations. Yet, the influence of molecular reorientations on the transfer process can have important consequences. It has been shown, for instance, that precise knowledge is required of the orientation factor in Förster type energy transfer rates, originating from dipole–dipole interactions between donor and acceptor, in order for these rates to serve as accurate spectroscopic rulers.[2] In this case, as perhaps in many other situations, the careless use of orientation factors pertaining to uniformly distributed orientations in the dynamic or static limit, appears to be totally inadequate.

It is the purpose of this work to provide a complete theoretical framework for inclusion of the orientation factor in Förster type transfer rates. In particular we calculate its effect upon the configuration averaged probability of finding an initially (optically) excited donor still to be excited at a later time. This quantity of central importance is, for instance, directly related to fluorescence depolarization caused by transfer of energy.[3] After giving a basic formulation of the problem and definitions of pertinent quantities in Sec. II, we obtain a general result for the excitation decay in two and three dimensions and for any axially symmetric distribution of molecular orientations (Sec. III). Effects of back transfer are also incorporated. From the general expression, essentially analytic results are derived for the dynamic and static limit in two and three dimensions and for arbitrary axially symmetric distributions of orientations (Sec. IV). In Sec. V the important question is discussed of deviations from these limits in the intermediate regime, when energy transfer and molecular reorientations take place on comparable time scales. In this case, analytic results can only be obtained for very short times. Therefore, we also attack the problem by means of computer simulations. We compare two qualitatively very different mechanisms of molecular reorientation, namely strong uncorrelated collisions and diffusion type reorientation. Section VI has the conclusions, together with a further discussion of previous and present results. Some technical results needed in Sec. V are contained in an appendix.

II. FORMULATION OF THE PROBLEM

Consider a medium in which excitation energy can be transferred incoherently between N, randomly embedded, molecules. Each molecule acts both as a possible donor and acceptor of energy, but will often for brevity be referred to as a "donor." Only axially symmetric molecules will be considered, with their centers of mass located at fixed positions in the medium. Hence each configuration of the system is characterized by the locations $(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ and the orientations $(\Omega_1, \Omega_2, \ldots, \Omega_N)$ of the donors. We will distinguish between the situations, where either the positions $\mathbf{r}_i$ can be chosen throughout three dimensional space, or they are all confined to one plane (two dimensional). In both cases, however, the orientational freedom is considered to be three dimensional. The angular distribution function $f(\Omega)$ of the donor orientations is thought to conform completely to that of the surrounding medium, which is assumed to be axially symmet-

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ric, and to possess a symmetry plane perpendicular to the symmetry axis (or director). If Ω_i is given as (θ_i, ϕ_i), where θ_i denotes the angle between the molecular axis and the director and ϕ_i is the azimuthal angle of the molecular axis in the symmetry plane, then the distribution function $f(\Omega)$ depends only on θ and can be expanded in Legendre polynomials P_L.[4]

$$f(\theta) = \sum_{\substack{L=0 \\ (L \text{ even})}}^{\infty} f_L \, P_L(\cos\theta) , \tag{2.1}$$

where

$$f_L = \frac{2L+1}{4\pi} \overline{P}_L \tag{2.2}$$

with $\overline{P}_L$ the average of P_L over the distribution f.

The incoherent transfer of energy is governed by the transfer rates w_{ij}, which fully determine coupled rate equations for the probabilities $\mathrm{P}_i(t)$ of finding donor i to be excited at time t in a given configuration

$$\frac{d\,\mathrm{P}_i}{dt} = -\sum_{j\neq i} w_{ij}(t)\mathrm{P}_i(t) + \sum_{j\neq i} w_{ji}(t)\mathrm{P}_j(t) . \tag{2.3}$$

Although the general theory presented in this work can easily be applied to other interactions, we will concentrate on the Förster rate of transfer between each pair (i,j) of molecules. This rate is due to dipole–dipole interaction and reads

$$w_{ij} = \tfrac{2}{3}\kappa_{ij}^2 \frac{1}{\tau}\left(\frac{R_0}{r_{ij}}\right)^6 , \quad r_{ij} = |\mathbf{r}_i - \mathbf{r}_j| . \tag{2.4}$$

Here τ is the excitation lifetime of a free molecule, and R_0 is the conventional critical transfer distance. The dependence on the orientations of the molecules is contained in the factor

$$\kappa_{ij}^2 = [\mathbf{e}_i \cdot \mathbf{e}_j - 3(\mathbf{e}_i \cdot \mathbf{e}_{ij})(\mathbf{e}_j \cdot \mathbf{e}_{ij})]^2 , \tag{2.5}$$

where $\mathbf{e}_i$ and $\mathbf{e}_j$ give the directions of the transition dipoles of molecule i and j, respectively, and $\mathbf{e}_{ij} = (\mathbf{r}_j - \mathbf{r}_i)/r_{ij}$. As the molecules are assumed to be axially symmetric, $\mathbf{e}_i$ always lies along the molecular axis and is thus determined by Ω_i. The polar coordinates of $\mathbf{e}_{ij}$ will be given by $\Omega_{ij} = (\theta_{ij}, \phi_{ij})$, with respect to the same frame as the orientation angles. In the two dimensional case $\theta_{ij} \equiv \pi/2$. In terms of these polar coordinates, the orientation factor (2.5) reads

$$\begin{aligned}\kappa_{ij}^2 &= \kappa^2(\Omega_i,\Omega_j;\Omega_{ij}) \\ &= \{\cos\theta_i \cos\theta_j + \sin\theta_i \sin\theta_j \cos(\phi_i - \phi_j) \\ &\quad - 3[\cos\theta_i \cos\theta_{ij} + \sin\theta_i \sin\theta_{ij}\cos(\phi_i - \phi_{ij})][i\leftrightarrow j]\}^2\end{aligned} \tag{2.6}$$

or, in yet another representation, that we will find useful sometimes,

$$\kappa_{ij}^2 = (1 + 3\cos^2\psi_1)\cos^2\psi_2 , \tag{2.7}$$

where ψ_1 is the angle between $\mathbf{e}_i$ and $\mathbf{e}_{ij}$, and ψ_2 is the angle between $\mathbf{e}_j$ and the electric field $\mathbf{f}$ of donor i, $\mathbf{f} = \mathbf{e}_i - 3(\mathbf{e}_i \cdot \mathbf{e}_{ij})\mathbf{e}_{ij}$. Since the donor positions are fixed in the medium, the transition rates depend on time only through the reorientational motion of the molecules, which is contained in κ_{ij}^2.

This work is primarily concerned with the effect of inclusion of this orientational factor upon the nonradiative excitation decay $\rho(t)$ which is for instance measured in TRFLN experiments[5] and also has a close relation to fluorescence depolarization.[3] As is well known, under quite general assumptions, this quantity is given by

$$\rho(t) = \langle \mathrm{P}_0^0(t) \rangle . \tag{2.8}$$

Here $\mathrm{P}_0^0(t)$ is the conditional probability, that an arbitrary donor "0" is still excited at time t, given the initial condition that only this donor is excited at $t = 0$, and $\langle \cdots \rangle$ denotes an appropriate average over donor configurations.

For donors of negligible volume, in an infinite system of dimension Δ, a scaling argument applies,[6] provided that the transfer rates are time independent. It states, that in a system of donor density n, ρ depends on n and t only through

$$T = \hat{n}^{6/\Delta}(t/\tau) , \tag{2.9}$$

where $\hat{n} = nV_\Delta R_0^\Delta$ is the average number of donors in a sphere of radius R_0, V_Δ being the volume of a Δ-dimensional unit sphere. In the following, ρ will often be expressed as a function of T, also when the scaling argument does not apply, in which case both T and t will occur in expressions for ρ.

As is clear from the coupled rate equations (2.3), the natural decay of the excitation is left out, since it only contributes an overall factor $\exp(-t/\tau)$ to $\rho(t)$.

III. GENERAL DESCRIPTION FOR $\rho(t)$

In order to give a complete description for the nonradiative decay $\rho(t)$, which even applies in the case of molecular reorientations, we will now derive an expression for this quantity by generalizing a model of Huber *et al.*[5] and the averaging procedure of Blumen and Manz.[7]

A straightforward extension of Huber *et al.* solution to Eq. (2.3) with initial condition $\mathrm{P}_i^0(0) = \delta_{i0}$ for a fixed donor configuration reads

$$\mathrm{P}_0^0(t) = \prod_{i\neq 0} \left[e^{-\langle w_{0i}\rangle_t \cdot t} \cosh(\langle w_{0i}\rangle_t \cdot t)\right] , \tag{3.1}$$

where i runs over all donors and

$$\langle w_{0i}\rangle_t = \frac{1}{t}\int_0^t w_{0i}(t')dt' \tag{3.2}$$

indicates the time averaged transfer rate between donor 0 and donor i. Equation (3.1) takes into account back transfer effects to first order in the donor density, and, in the case of time-independent transfer rates, has been proven to yield good approximations of the exact solution for $\rho(t)$.[8] The fact that Eq. (3.1) factorizes into separate contributions of all individual donors i makes it possible to generalize the averaging procedure of Blumen and Manz in order to derive $\rho(t)$. Note that the contribution of donor i depends only on $\langle w_{0i}\rangle_t$, which in view of the fixed donor positions, may be written as

$$\langle w_{0i}\rangle_t = \frac{1}{\tau}\left(\frac{R_0}{r_{0i}}\right)^6 K(\alpha_0,\alpha_i;\Omega_{0i},t) . \tag{3.3}$$

Here α labels all different types of donors, distinguished, for instance, by different reorientational motions, internal degrees of freedom or any other property which could influence the transfer between 0 and i. For the moment we choose α to be a discrete set, $\alpha = 1,2,\ldots,A$, which, however, is not necessary. The function K in Eq. (3.3) contains all depen-

dence of $\langle w_{0i} \rangle_t$ on the types of donors 0 and i, and also on the direction Ω_{0i} of their relative position. We assume, that the donor types are distributed, independently of the donor positions, according to a distribution function f_α, which is normalized to $\Sigma_{\alpha=1}^{A} f_\alpha = 1$.

We first consider the case that all initially excited donors in the system are of one type, say, α_0. Then the excitation decay will be denoted by $\rho_{\alpha_0}(t)$ and is obtained by averaging $P_0^0(t)$ in Eq. (3.1) over all possible distributions of donor types and their positions surrounding donor 0. The averaging can be performed easily by making the system discrete. (Later on, we will take the continuum limit of the discrete results.) So, let us consider a lattice, with sites labeled l, randomly occupied by the different types of donors, except for $l = 0$, which will be occupied by the initially excited donor of type α_0. The probability of a site to be occupied by a donor, regardless of its species, is denoted by c, so that the probability of finding a donor of type α on a given site is given by $f_\alpha c \equiv c_\alpha$. The probability of finding a site not occupied by a donor at all ("empty") will be $1 - c \equiv c_0$, and from now on we add type $\alpha = 0$ to the set of donor species, indicating an empty site. The new set of donors thus has a distribution function c_α ($\alpha = 0,\ldots, A$). If we define $K(\alpha_0,0;\Omega_{0l},t) = 0$, Eq. (3.1) becomes

$$P_0^0(t) = \prod_{l\neq 0} \left\{ \exp\left[-\frac{t}{\tau}\left(\frac{R_0}{r_{0l}}\right)^6 K(\alpha_0,\alpha_l;\Omega_{0l},t)\right] \times \cosh\left[\frac{t}{\tau}\left(\frac{R_0}{r_{0l}}\right)^6 K(\alpha_0,\alpha_l;\Omega_{0l},t)\right]\right\}, \tag{3.4}$$

where l is now running over all lattice sites, except 0. Following the procedure introduced in Ref. 7 it is found that the average fraction of lattice sites which are occupied by donor type α is given by c_α in the thermodynamic limit, and furthermore that

$$\rho_{\alpha_0}(t) = \prod_{l\neq 0} \sum_{\alpha=0}^{A} c_\alpha \left\{ \exp\left[-\frac{t}{\tau}\left(\frac{R_0}{r_{0l}}\right)^6 K(\alpha_0,\alpha_l;\Omega_{0l},t)\right] \times \cosh\left[\frac{t}{\tau}\left(\frac{R_0}{r_{0l}}\right)^6 K(\alpha_0,\alpha_l;\Omega_{0l},t)\right]\right\} \tag{3.5}$$

which reduces to

$$\rho_{\alpha_0}(t) = \prod_{l\neq 0} \left\{ (1 - \tfrac{1}{2}c) + \tfrac{1}{2}c \sum_{\alpha=1}^{A} f_\alpha \times \exp\left[-\frac{2t}{\tau}\left(\frac{R_0}{r_{0l}}\right)^6 K(\alpha_0,\alpha_l;\Omega_{0l},t)\right]\right\}. \tag{3.6}$$

Next, $\rho_{\alpha_0}(t)$ should be averaged over all possible kinds of initially excited donors. Let f'_α ($\alpha = 1,\ldots, A$) denote the fraction of initially excited donors that is of type α_0. Then

$$\rho(t) = \sum_{\alpha_0=1}^{A} f'_{\alpha_0} \rho_{\alpha_0}(t). \tag{3.7}$$

In the following we will always consider $f'_\alpha = f_\alpha$, i.e., equal probabilities of initial excitation for all donor species. Following Ref. 7 we now take the logarithm of Eq. (3.6), expand in powers of c and use a continuum approximation for $\Sigma_{l\neq 0}$ (leaving out any finite size effects of the donor molecules). For continuous media, we let $c \to 0$ and the site density $v \to \infty$, such that $cv = n =$ constant. One then obtains, together with Eqs. (3.5) and (3.6),

$$\rho(t) = \sum_{\alpha_0=1}^{A} f_{\alpha_0} \exp\left\{ -2^{\Delta/6-1}\Gamma\left(1-\frac{\Delta}{6}\right) T^{\Delta/6} \frac{1}{\Delta V_\Delta} \times \int d\Omega_r \sum_{\alpha=1}^{A} f_\alpha \left[K(\alpha_0,\alpha;\Omega_r,t)\right]^{\Delta/6}\right\}. \tag{3.8}$$

IV. DYNAMIC AND STATIC LIMIT

A. Dynamic limit

In the dynamic limit, molecular reorientations take place on a time scale very small compared to characteristic times for transfer of energy. Hence the donors sample the angular distribution induced by the medium completely before appreciable energy transfer occurs. Therefore the orientation factor (2.5) can be replaced by its average $\overline{\kappa_{ij}^2}$ over the angular distributions of the donors i and j:

$$\kappa_{\rm dyn}^2(\Omega_{ij}) = \overline{\kappa_{ij}^2}. \tag{4.1}$$

Thus the transfer rates (2.4) to be substituted in the rate equations (2.3) become time independent.

For general distributions of type (2.1) straightforward but tedious algebra yields $\frac{2}{3}\kappa_{\rm dyn}^2$ as a function of arbitrary order in the medium. The result is

$$\tfrac{2}{3}\kappa_{\rm dyn}^2(\Omega_{r_{ij}}) = \tfrac{2}{3}(a + b\cos^2\theta_{ij} + c\cos^4\theta_{ij}) \tag{4.2}$$

with

$$a = \tfrac{2}{3} - \tfrac{2}{3}\overline{P}_2 + \overline{P}_2^{\,2}, \tag{4.3a}$$

$$b = 2\overline{P}_2 - 8\overline{P}_2^{\,2}, \tag{4.3b}$$

$$c = 9\overline{P}_2^{\,2}. \tag{4.3c}$$

In the two-dimensional case, $\theta_{ij} = \pi/2$, and only a is of importance. Furthermore $\frac{2}{3}\kappa_{\rm dyn}^2$ is of course always independent of ϕ_{ij} because of axial symmetry, and depends on the distribution function only through $\overline{P}_2$. For the uniform (isotropic) distribution $\overline{P}_0 = 1$ and $\overline{P}_L = 0$ for all $L > 0$, hence $\frac{2}{3}\kappa_{\rm dyn}^2 = 1$ both in two- and three-dimensional systems. In this case there is no contribution of the orientation factor to the excitation decay $\rho(t)$, which is a well-known result.[9] The situation is somewhat different in partially ordered media ($\overline{P}_2 \neq 0$). If we use the general expression (3.8) for $\rho(t)$, we may now replace $K(\alpha_0,\alpha;\Omega_r,t)$ by $\frac{2}{3}\kappa_{\rm dyn}^2(\theta_r)$, which no longer depends on time and corresponds to the situation of only one type of donors present in the medium. Evaluation of Eq. (3.8) then gives

$$\log \rho_{\rm dyn}(t) = -2^{\Delta/6-1}\Gamma(1-\Delta/6)T^{\Delta/6} g_{\rm dyn} \tag{4.4}$$

with

$$g_{\rm dyn} = \frac{1}{\Delta V_\Delta}\int d\Omega_r \left[\tfrac{2}{3}\kappa_{\rm dyn}^2(\Omega_r)\right]^{\Delta/6}. \tag{4.5}$$

Substitution of Eqs. (4.2) and (4.3) yields

$$g_{\rm dyn} = (1 - \overline{P}_2 + \tfrac{3}{2}\overline{P}_2^{\,2})^{1/3} \qquad (2d), \tag{4.6}$$

$$g_{\rm dyn} = \sqrt{\tfrac{2}{3}}\int_0^1 dx (a + bx^2 + cx^4)^{1/2} \qquad (3d). \tag{4.7}$$

Both results are shown in Fig. 1. Particularly in two dimensions, sizable variations are possible depending on the degree

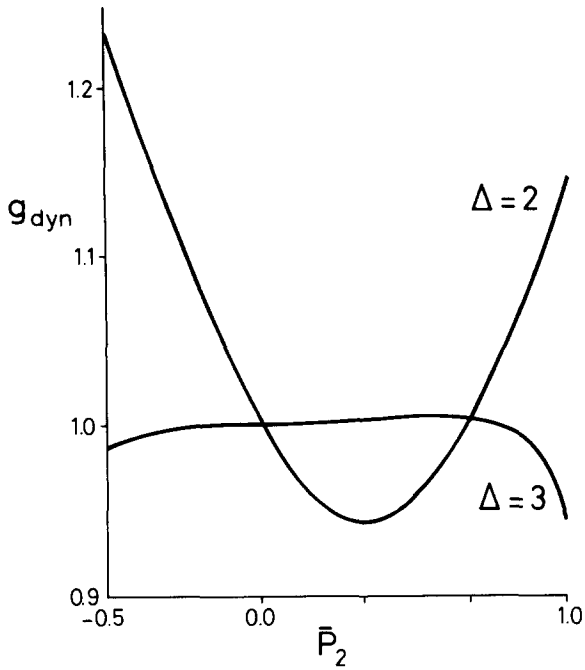

FIG. 1. The factor $g_{\rm dyn}$, occurring in expression (4.4) for $\log\rho(t)$ in the dynamic limit, as a function of arbitrary degree of orientational order ($\overline{P_2}$) in the medium.

of order. A striking difference between two and three dimensions lies in the fact that (in the dynamic limit) excitation decay in two dimensions is faster in ordered systems then in isotropic systems, while the reverse is true in three dimensions. From Eq. (4.4) it is furthermore observed, that $\rho_{\rm dyn}$ depends only on time through the variable T. Apparently the scaling argument does apply here, as could be expected, since the transfer rates become essentially time independent in the dynamic limit.

B. Static limit

In the opposite limit molecular orientations are considered to be fixed on time scales of interest for the transfer process, so that, again, the transfer rates become time independent. In this case, the general expression (3.8) may be used, by considering donors of different fixed orientation as different types. Now, of course, the set of types is continuous. Then, $K(\alpha_0,\alpha;\Omega_r,t)$ should be identified with $\frac{2}{3}\kappa^2(\Omega_0,\Omega;\Omega_r)$ and f_α corresponds to the angular distribution $f(\Omega)$. Hence, according to Eq. (3.8),

$$\rho_{\rm stat}(t)=\int d\Omega_0 f(\Omega_0)\exp\Big\{-2^{\Delta/6-1}\Gamma(1-\Delta/6)T^{\Delta/6}\times\frac{1}{\Delta V_\Delta}\int d\Omega_r\int d\Omega f(\Omega)\big[\tfrac{2}{3}\kappa^2(\Omega_0,\Omega;\Omega_r)\big]^{\Delta/6}\Big\}. \tag{4.8}$$

In general the integrals in Eq. (4.8) cannot be performed analytically because of the complicated form of κ^2.

A special case, in which Eq. (4.8) can be evaluated exactly, is the perfectly ordered medium. In this case the transition dipoles all point along the director, either up or down ($\theta=0$ or $\theta=\pi$, respectively). Since κ^2 is invariant under reflection in the origin [see Eq. (2.5)], Eq. (4.8) now reduces to the case of only one species and yields

$$\log\rho_{\rm stat}(t)=-2^{\Delta/6-1}\Gamma(1-\Delta/6)T^{\Delta/6}g_{\rm stat} \tag{4.9}$$

with

$$g_{\rm stat}=\sqrt[3]{\tfrac{3}{2}}\simeq 1.145 \quad (2d,\ \text{perfect order}), \tag{4.10}$$

$$g_{\rm stat}=\tfrac{2}{3}\sqrt{2}\simeq 0.943 \quad (3d,\ \text{perfect order}). \tag{4.11}$$

The results (4.9) with Eqs. (4.10) and (4.11) are exactly the same as the ones obtained in the dynamic limit for perfect order, Eq. (4.4) with Eqs. (4.6) and (4.7), which is not surprising since in this case the dynamic limit leads to stationary κ^2 values, as the orientations can only switch between two positions that leave κ^2 invariant.

Another special case, in which Eq. (4.8) can be evaluated exactly, is the isotropic case, but only in three dimensions. From symmetry arguments it follows that in this case the decay $\rho_{\Omega_0}(t)$ of a donor with orientation Ω_0 does not depend on Ω_0. Therefore, the averaging in Eq. (3.7) may be left out, and one obtains

$$\log\rho_{\rm stat}(t)=-2^{1/2}\Gamma(\tfrac{1}{2})T^{1/2}\frac{1}{4\pi}\int d\Omega_r\times\int d\Omega\frac{1}{4\pi}\big[\tfrac{2}{3}\kappa^2(\Omega_0,\Omega;\Omega_r)\big]^{\Delta/6} \tag{4.12}$$

[cf. Eq. (4.8)]. Ω_0 can be chosen arbitrarily in Eq. (4.12). By using expression (2.7) for κ^2, one easily obtains from Eq. (4.12),

$$\log\rho_{\rm stat}=-2^{1/2}\Gamma(\tfrac{1}{2})T^{1/2}g_{\rm stat} \tag{4.13}$$

with

$$g_{\rm stat}=\sqrt{\frac{3}{2}}\Big[\frac{1}{2}+\frac{1}{8\sqrt{3}}\log\Big(\frac{2\sqrt{3}+3}{2\sqrt{3}-3}\Big)\Big]\simeq 0.8452 \quad (3d,\ \text{isotropic}). \tag{4.14}$$

This is a well-known result.[9] In all other cases Eq. (4.8) cannot be tackled analytically. A way of gaining some further insight in the excitation decay is to evaluate $\rho_{\rm stat}$ for small T (which corresponds to small times or small densities). By expanding the exponent in Eq. (4.8) to first order in $T^{\Delta/6}$ one finds

$$\rho_{\rm stat}\simeq 1-2^{\Delta/6-1}\Gamma(1-\Delta/6)T^{\Delta/6}g_{\rm stat} \tag{4.15a}$$

or, alternatively,

$$\log\rho_{\rm stat}\simeq -2^{\Delta/6-1}\Gamma(1-\Delta/6)T^{\Delta/6}g_{\rm stat} \tag{4.15b}$$

with

$$g_{\rm stat}=\frac{1}{\Delta V_\Delta}\int d\Omega_r\int d\Omega\int d\Omega_0 f(\Omega)f(\Omega_0)\times\big[\tfrac{2}{3}\kappa^2(\Omega_0,\Omega;\Omega_r)\big]^{\Delta/6}, \tag{4.16}$$

where the g notation is used as an extension of the above exact results. Clearly Eq. (4.16) represents the average of $(\kappa^2)^{\Delta/6}$ over all angular distributions of interest to κ^2. Note, that Eq. (4.15b) with Eq. (4.16) has the same structure as the exact results obtained earlier, since it factorizes in the general form $-2^{\Delta/6-1}\Gamma(1-\Delta/6)T^{\Delta/6}$ and a time-independent factor $g_{\rm stat}$ which is fully determined by the degree of order and the dimension. For the special case of a two-di-

mensional isotropic system (4.16) is evaluated numerically. One finds

$$g_{\text{stat}} \simeq 0.8468 \quad (2d,\ \text{isotropic}) \tag{4.17}$$

which is remarkably close to the value (4.14) in three dimensions.

V. INTERMEDIATE REGIME

Let τ_a designate the time scale for molecular reorientations. Then $\rho(t)$ will be given by the static limit if $t \ll \tau_a$, and by the dynamic limit if $t \gg \tau_a$, as discussed in the previous section. In the intermediate time regime $\rho(t)$ must undergo a transition between these two limits. Evidently, from a theoretical point of view, a realistic system (finite τ_a) passes all three time regimes mentioned above, regardless of the ratio of τ_a to a typical transfer time. This ratio, however, determines, whether it is possible to observe all three regimes in an experiment. In the limiting cases, $\log \rho(t)$ always has the general form $-2^{\Delta/6-1}\Gamma(1-\Delta/6)T^{\Delta/6}g$, where g is a time-independent factor (Sec. IV). In the intermediate regime, however, g becomes time dependent, thus perhaps significantly altering the overall time dependence of the excitation decay. Moreover, the time dependence in the intermediate regime may yield useful information on the mechanism of reorientation. We are therefore motivated to determine $\rho(t)$ beyond the limiting cases for different models of molecular reorientation.

Again, we use the general description of $\rho(t)$ given in Eq. (3.8). The quantity $\langle w_{0i} \rangle_t$ in Eq. (3.3) is fully determined by the position of donor i with respect to donor 0, and by the reorientational motions of donors 0 and i in the time interval $(0,t)$, hereafter to be called the trajectories and denoted by ξ_0 and ξ_i, respectively. Therefore it is appropriate to identify the set of donor species with the (tremendously complicated) set of all possible trajectories, so that $K(\alpha_0,\alpha_i;\Omega_{0i},t)$ must be replaced by $\langle \frac{2}{3}\kappa^2[\Omega(\xi_0),\Omega(\xi_i);\Omega_{0i}]\rangle_t$. Then Eq. (3.8) becomes

$$\rho(t) = \sum_{\xi_0} f_{\xi_0} \exp\Bigg(-2^{\Delta/6-1}\Gamma(1-\Delta/6)T^{\Delta/6} \times \frac{1}{\Delta V_\Delta} \int d\Omega_r \sum_{\xi} f_\xi \times \left\{ \langle \tfrac{2}{3}\kappa^2[\Omega(\xi_0),\Omega(\xi);\Omega_r]\rangle_t \right\}^{\Delta/6} \Bigg). \tag{5.1}$$

It is easily seen how this result reduces to the limits (4.4) and (4.8), respectively, discussed in Sec. IV. In the dynamic limit, the entire angular distribution will be sampled by any pair of trajectories in the interval $(0,t)$, while in the static limit the trajectories are completely determined by the initial orientations, taken randomly from the angular distribution. In the intermediate regime, however, exact evaluation of Eq. (5.1) is impossible. Therefore the exponent in Eq. (5.1) is first expanded for small T, which yields the familiar form

$$\log \rho(t) \simeq -2^{\Delta/6-1}\Gamma(1-\Delta/6)T^{\Delta/6}g(t/\tau_a), \tag{5.2}$$

where $g(t/\tau_a)$ is now a *time-dependent* factor, given by

$$g(t/\tau_a) = \frac{1}{\Delta V_\Delta} \int d\Omega_r \sum_{\xi_0} \sum_{\xi} f_\xi f_{\xi_0} \times \left\{ \langle \tfrac{2}{3}\kappa^2[\Omega(\xi_0),\Omega(\xi);\Omega_r]\rangle_t \right\}^{\Delta/6}. \tag{5.3}$$

Except for small times, this factor can still be evaluated only numerically. We write g as a function of t/τ_a, since it is determined by reorientations, for which τ_a is a natural time scale. Because the transfer rates are now time dependent, the scaling argument is not valid anymore, as is clear from Eq. (5.2). Note that the small T expansion does not imply a restriction to small times. Therefore it may indeed be possible to reach the intermediate regime and the dynamic limit in a time interval where the small T expansion is still valid. The advantage of the approximation (5.2) over the exact result (5.1), lies in the fact, that the entire contribution of reorientations to the excitation decay is contained in the factor g.

We discuss two qualitatively different models of molecular reorientation, strong collisional reorientation and diffusive reorientation. In both cases the molecular orientation is assumed to change suddenly (jump), i.e., to take place in a time negligibly small compared to the mean time spent between reorientations. This mean time provides us with a natural time scale τ_a for reorientation, and the probability that a molecule has not jumped in the time interval $(0,t)$ is now given by e^{-t/τ_a}. The essential difference between the two models lies in the correlation between the orientation before and after the jump. In the case of strong collisions there is no correlation at all,[10] i.e., the new orientation is taken completely random from the angular distribution $f(\Omega)$. In the diffusion model it is assumed that the molecule can only jump to positions within an angle $\theta_{\max}$ from the old orientation, while maintaining the distribution $f(\Omega)$. It is clear, that for $\theta_{\max} = \pi$, the diffusion model is equivalent with the strong collision model.

Evaluation of Eq. (5.3) requires time averaging for fixed trajectories ξ_0 and ξ, followed by taking the averages over all trajectories and the direction of the position of the acceptor with respect to the donor. Generally, however, the distribution f_ξ for the trajectories is so complicated, that an exact integration is impossible. Therefore, a simulation technique is developed, which, in combination with a Monte Carlo integration, approximates $g(t/\tau_a)$. The problem is simplified by going to a discrete set of moments at which reorientations can occur. The interval $(0,t)$ is therefore broken up into k small intervals, separated by the moments $i \cdot t/k$, $i = 1,2,\ldots,k-1$. In accordance with the e^{-t/τ_a} law for the orientation to remain unchanged, a molecule has now at each of these moments a probability, $p = 1 - \exp\{-t/[(k-1)\tau_a]\}$ to make a jump. Now each trajectory is given by specifying the finite set of moments at which a jump is actually made (which we will call the "base," b, of the trajectory), together with the initial orientation and the new orientation after every jump. It is clear that the smaller the time intervals $t/k\tau_a$ are chosen, the more accurate this procedure will be. In our calculations it turns out, that k should at least equal $2t/\tau_a$ in order not to influence the accuracy imposed by the numerical integrations. The average over the distribution of trajectories now separates into an average over the different orientations that can be encoun-

tered for a given pair of bases and a subsequent average over the bases. Then Eq. (5.3) is replaced by

$$g = \sum_{b_0} \sum_{b} \mathcal{P}(b_0)\mathcal{P}(b)\langle\langle \tfrac{3}{2}\kappa^2\rangle_t^{\Delta/6}\rangle_{\text{ang}} , \tag{5.4}$$

where $\mathcal{P}(b)$ denotes the probability for base b to occur, and $\langle\cdots\rangle_{\text{ang}}$ denotes the average over the orientations and over Ω_r. For every pair (b_0,b) of bases $\langle\cdots\rangle_t$ is a unique, and in fact a known function of the orientations, and $\langle\cdots\rangle_{\text{ang}}$ is given by a $2j+6$-dimensional integral, where j is the number of jumps that are made by either the donor or the acceptor.

It is clear, that, even for moderately large k, the number of possible bases is very high (viz. $2^{2(k-1)}$), so that the number of integrals $\langle\cdots\rangle_{\text{ang}}$ to be performed is too large. Therefore the sums Σ_{b_0} and Σ_b in Eq. (5.4) are not evaluated exactly, but the distributions f_ξ and f_{ξ_0} are sampled by a simulation. As the individual jump probabilities p are known for given time t/τ_a and a choice of k, two bases b_0 and b can be taken from their distribution by means of a random number generator. Subsequently, $\langle\cdots\rangle_{\text{ang}}$ for these bases is determined by Monte Carlo integration, where we restrict our attention to the isotropic case $[f(\Omega) = 1/4\pi]$. For the strong collision model, the orientations themselves are the suitable integration variables, since they are completely independent. For the diffusion model, however, it is more convenient to replace the two-dimensional integration over orientations after every jump, by an, also two dimensional, integration over new variables $\cos\tilde{\theta}$ and $\tilde{\phi}$, which specify the jump and can be chosen in a uniform and random way in the intervals $(\cos\theta_{\max},1)$ and $(0,2\pi)$, respectively.[11] It turns out, that the Monte Carlo integration can be performed with an accuracy of about 0.5% by choosing 3×10^4 random points in the $2j+6$-dimensional integration space.

The calculation of $\langle\cdots\rangle_{\text{ang}}$ is repeated for different choices of bases. By averaging the resulting integrals an approximation for g is obtained. The number of bases to be chosen in order to maintain an accuracy of about 0.5% turns out to be very low (± 40) compared to the usually very large number of possible bases. This can be understood by observing that many bases, though not completely the same, may yield time averages that are very similar, as a function of the orientations.

The above method is used to determine $g(t/\tau_a)$ in two and three dimensions for the strong collision model and the diffusion model with $\theta_{\max} = 30°$ and $\theta_{\max} = 12°$, respectively. It is evident, that the transition from static to dynamic limit will occur faster as a function of t/τ_a for larger $\theta_{\max}$ and will be fastest for the strong collision model. The simulations confirm this. This, by itself, is however not the most interesting difference between the models, since if one is able to measure $g(t)$, τ_a will presumably not be known, so that one is not able to extract $g(t/\tau_a)$ directly from experimental data. A more interesting difference therefore lies in the shapes of the curves $g(t/\tau_a)$ for different models. These are most conveniently compared by using the behavior of $g(t/\tau_a)$ for very small t/τ_a. In an Appendix, this behavior is studied in an essentially analytic way up to first order of t/τ_a, by considering only pairs of trajectories ξ_0 and ξ, where the donor and acceptor are both stationary or at most one of them jumps once (single jump approximation). It turns out that for every $\theta_{\max}$ (including the strong collision case $\theta_{\max} = \pi$), the initial slope $m = [dg(t/\tau_a)]/[d(t/\tau_a)]|_{t=0}$ differs from zero. Its value can be calculated by a Gaussian quadrature.

TABLE I. Initial slopes $m = [dg(t/\tau_a)]/[d(t/\tau_a)]|_{t=0}$ for the three different models treated in Sec. V, both in two and three dimensions. The theory needed to evaluate m is given in the Appendix.

	$\Delta = 3$	$\Delta = 2$
Strong collision	0.102 39	0.110 71
Diffusion, $\theta_{\max} = 30°$	0.031 36	0.038 79
Diffusion, $\theta_{\max} = 12°$	0.007 83	0.011 33

Now the shapes of the curves can be compared unambiguously by rescaling the time t, so that all initial slopes equal a fixed value. Fundamental differences between the curves, that can be identified also experimentally by adjusting the initial slope, will then show up for larger rescaled times. We chose as fixed slopes the values for strong collisions, which are given in Table I, together with the values for $\theta_{\max} = 30°$ and 12°, respectively. Note how small the difference is between the values in two and three dimensions. The factors, by which the time must be compressed to adjust the initial slopes, are now easily calculated. The initial slopes, calculated from our simulations, appear to be in good agreement with the theoretical values.

After rescaling, the curves in Fig. 2 are obtained from the simulations for $\Delta = 3$. The following conclusions can now be drawn: (i) The numerical results reproduce, of course, the static and dynamic (only shown for the case of strong collisions) limits, which serves as a check for our calculational procedure. (ii) Whereas the differences in the shapes of the curves for various $\theta_{\max}$ are not dramatic, it can still be concluded, that, the more diffusive the reorientational motion becomes ($\theta_{\max}$ smaller), the lower the curves $g(t)$ (with adjusted initial slope) will lie. Therefore Fig. 2 provides in fact an accurate set of reference curves, which may be very useful for estimating the amount of diffusive character present in the reorientational motion. Furthermore, once $\theta_{\max}$ is estimated, one is able to calculate m, which, together

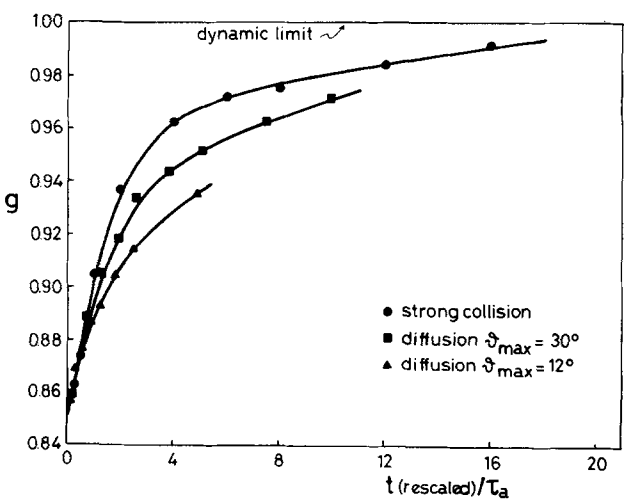

FIG. 2. Numerical results of g as a function of time for three different models of molecular reorientation. For the two diffusion models, time is rescaled in order to obtain the same initial slope as in the case of strong collisions.

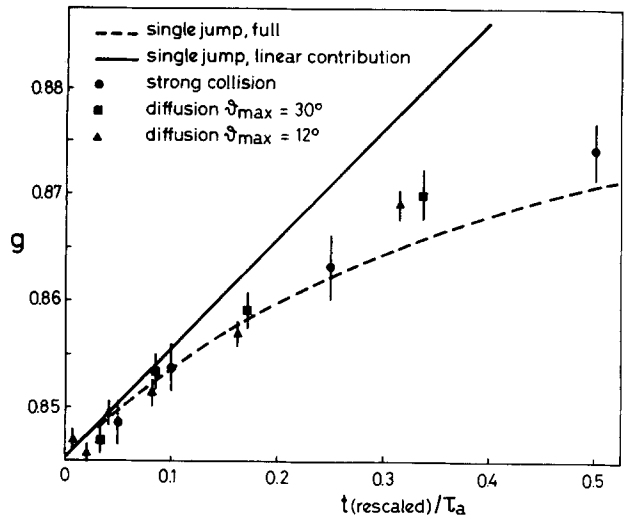

FIG. 3. Same as Fig. 2, but now for small times. In addition the full single jump approximation to $g(t)$ is given [see Eq. (A8)], and its linear contribution.

with the experimental data, can be used to estimate τ_a. (iii) The rescaled numerical data for small times ($t/\tau_a \lesssim 0.5$) are indeed seen to fall on one single curve, regardless of θ_{max}. For very small times ($t/\tau_a \lesssim 0.1$), this curve is given by the linear single jump contribution and for somewhat higher times by the full single jump approximation (see the Appendix). This is illustrated in more detail by Fig. 3. The results for $\Delta = 2$ are not displayed here, because they are found to be basically the same.

A further, very striking, difference between models for different θ_{max} is shown in Fig. 4. Here the distributions N are given of $\langle\langle\frac{3}{2}\kappa^2\rangle_t^{\Delta/6}\rangle_{ang}$ (hereafter denoted as $\langle\cdots\rangle_{ang}$) for different (not rescaled) times for the three models studied numerically in three dimensions. These distributions are determined by considering the values of $\langle\cdots\rangle_{ang}$ for the different bases chosen at random in the simulation. N is given in arbitrary units and all distributions are normalized to the same total area. It is visualized here once again, that the mean value of the distribution (which equals g) increases faster for larger θ_{max}. More interesting, however, are the differences in the shape evolutions of the distributions. For the strong collision model for early times ($t/\tau_a \simeq 0.1$–2) the sharp initial peak at g_{stat} slowly declines and an entirely separated peak shows up at intermediate values of $\langle\cdots\rangle_{ang}$, which grows at the expense of the initial peak. This is clearly a result of the occurrence of trajectories with one or even more jumps over large angles. The second, relatively broad, peak, which might even be separated into different peaks for different numbers of jumps, slowly moves to higher values. For larger times it gets sharper again, illustrating that, indeed, for any pair of trajectories the dynamic limit is approached.

In the opposite case of strong diffusive behavior ($\theta_{max} = 12°$) the distribution also starts as a sharp peak at g_{stat}, but now moves to higher values without breaking up, and stays relatively sharp. This is understood, by noting, that the jump angles are too small for an entirely separated peak to develop at small times. For $\theta_{max} = 30°$ obviously an intermediate case is illustrated, where the initial peak is broadened strongly, but does not yet break up. It is clear from these figures, that, whereas the value for g may be the same for different models (at different times), the underlying distribution picture may be totally different. For two dimensions the results are again very much alike. However amusing these features are, it seems hard to determine these distri-

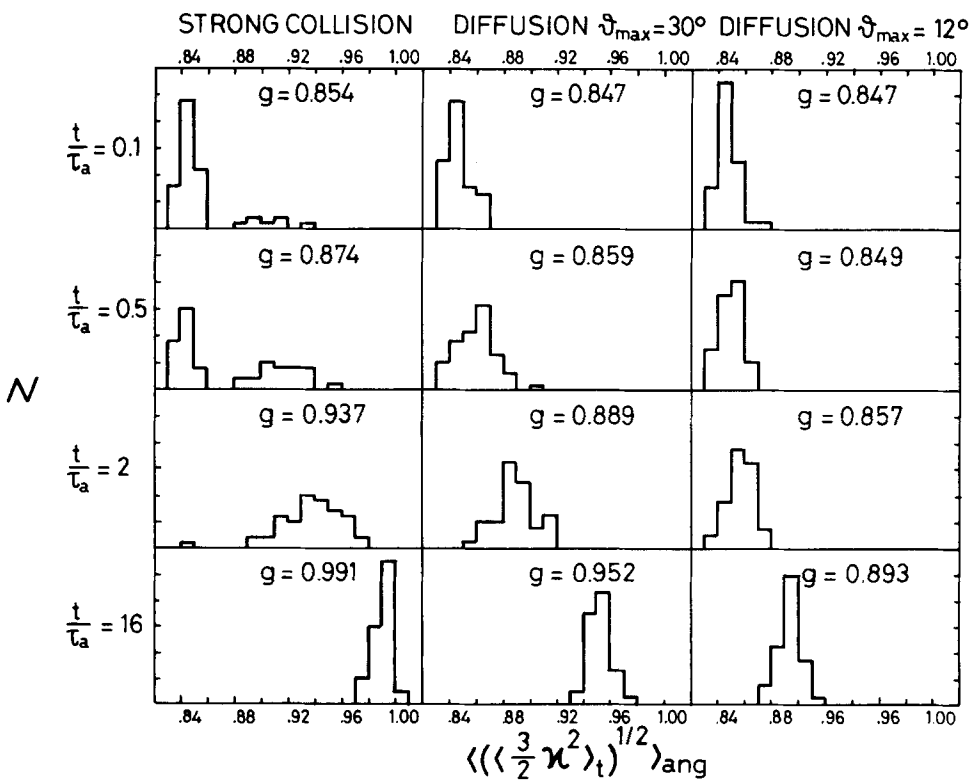

FIG. 4. Time evolution of the distributions N of $\langle\langle\frac{3}{2}\kappa^2\rangle_t^{\Delta/6}\rangle_{ang}$ for three different models obtained from our simulations for three dimensions (time not rescaled). Arbitrary units are used, and all distributions are normalized to the same total area.

butions experimentally, so that the practical value will probably be limited.

VI. SUMMARY AND CONCLUSIONS

In this work a study of excitation decay due to the anisotropic Förster transfer is presented, that unlike most other work done in this field, accounts for finite reorientation times. The entire influence of the reorientational motion on the decay is shown to be contained in a time dependent factor $g(t/\tau_a)$, which is evaluated, for different models of reorientation, using a simulation technique. By means of a rigorous rescaling procedure, based on an exact expression of $g(t/\tau_a)$ for small t/τ_a, it is shown, that, in principle, experimental determination of $g(t)$ can be used to determine the amount of diffusive behavior in the reorientational motion and estimate τ_a. Expressions for the static and dynamic limits, which are well known for the isotropic case, are obtained as special cases from our general theory for arbitrary angular distributions. From these, exact results are obtained for the dynamic limit as a function of the degree of orientational order, in both two and three dimensions, and for the static limit in the isotropic case and the case of perfect order.

Of course, if a system can be made dilute (which may not be the case, for instance, if one wants to study it in some natural composition) information on molecular reorientation may be obtained more readily through fluorescence depolarization experiments, in which energy transfer can be neglected.[12] However, in such studies theoretical uncertainties may arise in the determination of the orientational relaxation time (e.g., regarding the microscopic description of viscosity). Therefore, while the main objective of this work is the investigation of excitation decay due to transfer in the regime between static and dynamic limit, we believe that results, such as obtained here, may yield useful additional information on the rotational dynamics of molecules.

As far as we know, other work done in the intermediate regime is carried out to describe steady-state experiments (instead of the flash excitation we considered). Bojarski and Dudkiewicz[13] introduced an *ad hoc* interpolation between the static and dynamic limit, which depends on the ratio of time scales for transfer and reorientation. A similar interpolation for g, using the ratio t/τ_a instead, yields

$$g(t/\tau_a) = \frac{1}{1+t/\tau_a} g_{\text{stat}} + \frac{t/\tau_a}{1+t/\tau_a} g_{\text{dyn}} ,$$

which, after adjusting the initial slope, closely follows our results for the case of strong collisions. In a more systematic study Dudkiewicz and Bojarski[14] derive an expression for the luminescence quantum yield of a solution in which restricted rotations of the molecules are allowed. This expression contains a time and distribution average of κ^2, which, at first sight, much resembles our "double" average of κ^2 in g. However, their time average is taken over a fixed averaged time of localization of the excitation on a donor, which cannot be justified in a random system. The work of Dale *et al.*,[2] already mentioned in the Introduction, however useful in combination with experiments, is very crude in its theoretical aspects, since it only yields lower and upper bounds for the averaged orientation factor.

We will now estimate roughly the time domain where experiments involving this theory can be carried out. Let us take $T \simeq 0.1$ (which corresponds to $\rho \simeq 0.67$) as a value typical of the region in which the overwhelming part of the decay takes place. Therefore, information on ρ as a function of t will be obtained in experiments which probe for times $t \simeq 0.1\tau/\hat{n}^{6/\Delta}$. From this it is easily seen, that, if τ_a is much greater (much smaller) than $0.1\tau/\hat{n}^{6/\Delta}$, the whole experiment will be carried out in the static (dynamic) limit. Only if $\tau_a \simeq 0.1\tau/\hat{n}^{6/\Delta}$, the intermediate regime will be observed. A further restriction to the time domain, in order for our theory to be applicable, is imposed by the small T expansion, which is reasonable only for $T \lesssim 0.1$. Finally it is clear that the overall natural decay $e^{-t/\tau}$ should not be too fast compared to the transfer decay, which gives $\tau \gtrsim 0.1\tau/\hat{n}^{6/\Delta}$ or $\hat{n}^{6/\Delta} \gtrsim 0.1$.

Experimental determination of $g(t)$ can probably be carried out with greater accuracy if the decay curve $\rho_{\text{order}}(t)$ for the same system in the case of perfect order (low temperature experiments) is used as a reference curve, since then $\log \rho(t)/\log \rho_{\text{order}}(t)$ directly yields $g(t)$. Another benefit of this method lies in the fact that a slight deviation in the overall $T^{\Delta/6}$ decay, caused by contributions of higher order multipole–multipole transfer rates (leading to an effective power not exactly $\Delta/6$) is separated from $g(t)$. Note from our results for $\Delta = 2$ and $\Delta = 3$, that the theoretical predictions of g itself are not very sensitive to the exact value of this power.

The theory, presented here, accounts for back transfer in a way analogous to the model of Huber *et al.*,[5] which is justified by its very good results.[8] It is not clear, however, whether this procedure can be justified in our general case just as well. Of course our theory can be used, without restrictions, in the case of a small number of donors, surrounded by a majority of traps, which give no back transfer at all. For this case T should be replaced by $2^{6/\Delta-1}T$[15] in expressions for $\rho(t)$, n will then denote the trap density.

It would be interesting to study the orientation factor for other systems. For a system in which all molecules precess around the director we find, that $g(t/\tau_a)$ is no longer a strictly increasing function of t/τ_a. An interesting problem would be the investigation of the effect on g of orientational order in the medium, for instance in view of application to fluorescence depolarization in membranes. Although the general theory presented here also includes ordered systems, we have not performed any simulation of g so far, because of the enormous computational effort involved.

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It is a pleasure to thank Y. K. Levine for drawing our attention to this problem.

APPENDIX

In this Appendix an essentially analytic study of the behavior of $g(t/\tau_a)$ for small t/τ_a is presented. Evidently, for small t/τ_a the overwhelming contribution to Eq. (5.3) is due to pairs of trajectories (ξ_0, ξ), where both donor and acceptor do not jump at all. To first order in t/τ_a, however, there will be pairs of trajectories where one of them changes

its orientation once. In the first (static) case the joint probability $f_{\xi_0} f_{\xi}$ is given by

$$C \cdot e^{-2t/\tau_a} f(\Omega_0) f(\Omega)\, d\Omega_0\, d\Omega\,, \tag{A1}$$

where $d\Omega_0 (d\Omega)$ is the small solid angle around $\Omega_0(\Omega)$ in which the donor (acceptor) orientation lies. C is a normalization constant. In the case of a single jump the probability is given by

$$2C \cdot e^{-2t/\tau_a} f(\Omega_0) f(\Omega)\, \tilde{f}(\Omega')\, d\Omega_0\, d\Omega\, d\Omega'\, \frac{dt_1}{\tau_a}\,, \tag{A2}$$

where Ω' denotes the acceptor orientation after the jump, which occurs within the time element dt_1 at t_1 $(0 < t < t_1)$. Note, that in contrast to the case of more jumps the time can now be dealt with continuously. The distribution $\tilde{f}(\Omega')$ equals $f(\Omega')$ in the case of strong collisions, whereas, in the case of diffusion it also depends on Ω. The factor of 2 in Eq. (A2) arises from the fact that a donor jump gives the same contribution as an acceptor jump. Neglecting the possibility of two or more jumps, it follows from Eqs. (A1) and (A2) that

$$C = \frac{e^{2t/\tau_a}}{1 + 2t/\tau_a}\,. \tag{A3}$$

Combining Eqs. (5.3), (A1), and (A2) one obtains as the single jump approximation

$$g = \frac{1}{1 + 2t/\tau_a} g_{\text{stat}} + \frac{2t/\tau_a}{1 + 2t/\tau_a} I\,, \tag{A4}$$

where I represents the integral

$$I = \frac{1}{\Delta V_\Delta} \int d\Omega_0 \int d\Omega \int d\Omega' \int d\Omega_r \int_0^1 ds\, f(\Omega_0) f(\Omega) \tilde{f}(\Omega') \times [s\kappa^2(\Omega_0, \Omega; \Omega_r) + (1-s)\kappa^2(\Omega_0, \Omega'; \Omega_r)]^{\Delta/6}\,. \tag{A5}$$

As in Sec. V, we restrict our attention to the isotropic case $f \equiv 1/4\pi$. Then, with notation (2.7) for κ^2, Eq. (A5) reduces to

$$I = \int \frac{d\cos\psi_1}{2} \left[\tfrac{3}{2}(1 + 3\cos^2\psi_1)\right]^{\Delta/6} \int \frac{d\cos\psi_2}{2} \times \int d\cos\psi_2'\, \tilde{f}(\psi_2') \int_0^1 ds \left[s\cos^2\psi_2 + (1-s)\cos^2\psi_2'\right]^{\Delta/6} \tag{A6}$$

or,

$$I = (1 + \Delta/3) g_{\text{stat}} K\,, \tag{A7}$$

where the last three integrals in Eq. (A6) are denoted by K, so that

$$g\left(\frac{t}{\tau_a}\right) = g_{\text{stat}} \left\{1 + \frac{2t/\tau_a}{1 + 2t/\tau_a} \left[\left(1 + \frac{\Delta}{3}\right) K - 1\right]\right\}. \tag{A8}$$

From Eq. (A8) it is clear that the initial slope $[dg(t/\tau_a)]/(dt/\tau_a)|_{t=0}$ is given by

$$m = 2g_{\text{stat}} [(1 + \Delta/3) K - 1]\,. \tag{A9}$$

Evaluation of K is simplest in the case of strong collisions, since then $\tilde{f}(\psi_2')$ is simply $\frac{1}{2}$. For $\Delta = 3$ an exact analytic result is obtained, for $\Delta = 2$ a Gaussian quadrature is used. The results read

$$m = 2g_{\text{stat}} (\tfrac{8}{9} \log 2 - \tfrac{5}{9}) \simeq 0.1024 \quad (3d,\ \text{strong}) \tag{A10a}$$

and

$$m \simeq 0.1107 \quad (2d,\ \text{strong})\,. \tag{A10b}$$

For the case of diffusion, K can be evaluated by using the fact that the acceptor orientation after the jump must be chosen in a uniform and random way within an angle $\theta_{\max}$ of the old orientation. The jump can be represented by auxiliary variables[11] $\cos\tilde{\theta}$ and $\tilde{\phi}$, distributed uniformly on $(\cos\theta_{\max}, 1)$ and $(0, 2\pi)$, respectively. Then the ψ_2' integration in Eq. (A6) can be rewritten in terms of integrations of $\cos\tilde{\theta}$ and $\tilde{\phi}$, using $\cos\psi_2' = \cos\psi_2 \cos\tilde{\theta} + \sin\psi_2 \sin\tilde{\theta} \cos\tilde{\phi}$, so that K becomes a four-dimensional integral, which is again determined by numerical integration for any value of $\theta_{\max}$. Specific results for m obtained in this way are presented in Sec. V.

Evidently, Eq. (A8) contains all contributions of $g(t/\tau_a)$ to first order in t/τ_a. Moreover, it gives a second order contribution, due to the denominator $[1 + 2(t/\tau_a)]^{-1}$. Although other second order effects are neglected (occurrence of two jumps), our simulation results (Sec. V) show that the full single jump approximation, defined by Eq. (A8), accounts well for nonlinear contributions in the time interval $t/\tau_a \lesssim 0.5$.

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[11] For an isotropic distribution a random diffusion step ($< \theta_{\max}$) is made by first rotating the initial orientation about an appropriate axis to a position parallel to the director. Then one chooses an intermediate orientation $(\tilde{\theta}, \tilde{\phi})$, by taking $\cos\tilde{\theta}$ and $\tilde{\phi}$ in a uniform and random way from the intervals $(\cos\theta_{\max}, 1)$ and $(0, 2\pi)$, respectively. Application of the inverse of the above rotation to $(\tilde{\theta}, \tilde{\phi})$ then gives a possible new orientation, expressed in terms of $\tilde{\theta}, \tilde{\phi}$ and the initial orientation.

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[15] In this case the factor cosh(...) does not appear in Eq. (3.5). Hence in Eq. (3.6) $\frac{1}{2}c$ and the factor of $2t$ in the exponent are replaced by c and t, respectively. This, in turn, leads to the replacement of T in Eq. (3.8) by $2^{6/\Delta - 1}T$.